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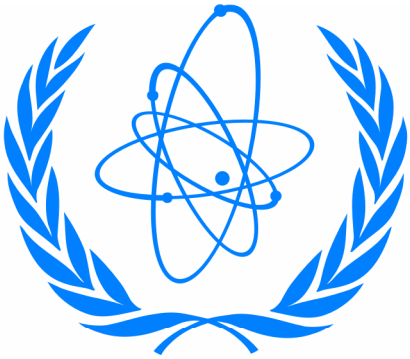
Report on the Proficiency Test Exercise for Analytical Laboratories Involved in Air Pollution Studies - PTXRFIAEA/03

Seibersdorf, November 2006

REPORT
ON
THE PROFICIENCY TEST EXERCISE
FOR
ANALYTICAL LABORATORIES INVOLVED IN AIR POLLUTION STUDIES
ORGANIZED BY
INTERNATIONAL ATOMIC ENERGY AGENCY
PTXRFIAEA/03



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FOREWORD

The proficiency test (code PTXRFIAEA03) was organized in response to a request of the analytical laboratories involved in two regional Technical Cooperation projects on Assessment of Atmospheric Pollution by Particles in Latin America (RLA/7/011) and Air Pollution Monitoring in the Mediterranean Region (RER/8/009). The participants of the projects are using nuclear analytical techniques to determine the elemental composition of fine (PM2.5) and coarse (PM10) particles in air particulate matter. The analytical results are used for identification of pollution sources and source apportionment in support of air quality management.

INTRODUCTION

The PTXRFIAEA03 proficiency test was aimed at the analytical laboratories applying nuclear analytical techniques (NAT) in air pollution studies. The participants were requested to use their established and proven analytical techniques for the determination of concentrations of all possible chemical elements. The samples, together with instructions for analysts, were distributed to the participating laboratories in December 2005. The deadline for submission of the results was March 31, 2006. The last results were received in June 2006. The submitted results were processed, grouped versus analytes/laboratories and compared with the analytes' assigned values. For each submitted result a set of *z*-scores and *u*-scores was calculated. The obtained results and description of the statistical evaluation procedures are presented in this report. Each laboratory was assigned a code, therefore full anonymity of the results presented in this report is guaranteed. The link between the laboratory code and the laboratory name is known only to the organizers of the proficiency test and to the laboratory itself.

DEFINITIONS AND TERMINOLOGY

In this section the definitions of terms used in the proficiency testing schemes are provided. Although this terminology might be known to the participants or can be found elsewhere [1-3] the terms used in this report are clearly defined to avoid any ambiguity:

Proficiency Testing Scheme: method of checking laboratory performance by means of inter-laboratory tests, sometimes called "round robin study".

True Value: the actual concentration of the analyte in the matrix.

Assigned Value: the value of the concentration of the analyte in the matrix used as the true value by the proficiency testing coordinator in the statistical treatment of results (or the best available estimate).

Target Value for Standard Deviation: a numerical value for the standard deviation of a measurement result, which has been designated as a target for measurement quality.

Consensus value: the mean value of the reported laboratory results after the removal of outliers.

Consensus value of the standard deviation: the standard deviation of the mean value of the reported laboratory results after the removal of outliers.

Certified Reference Material: A reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence.

DETAILS

Test Sample

The test sample was the IAEA candidate reference material IAEA-NAT-3, Urban Dust Artificially Loaded on Air Filters. Urban dust material was collected from the air conditioning system of the Vienna General Hospital (AKH) in Vienna, Austria. Approximately 9 kg of material were collected in three batches over the period September 1994 to December 1995. The batches of material were combined and sieved to particle fraction less than 70 μm. A portion of this material was then air-jet milled three times at the Agency's Laboratories Seibersdorf. The product has a peak particle size of 3.2 μm and a size range (FWHM) of 2.5 μm. This material was used to load the filters. The loading was performed under normal laboratory conditions at the Agency's Laboratories Seibersdorf. A Mastersizer X (Malvern) particle size measurement device equipped with a water bath, ultra sound stirrer and mechanical mixer, was used to prepare the water suspension of the material and to control the particle size and concentration of the material during the loading process. The starting material (16-20 mg) of urban dust was added to 1 L of double-distilled water with added surfactant (TRITON X-100, 0.1% v/v). The material was preconditioned for 1 hour. The sample was then kept continuously circulating through the measuring cell. Between the measuring cell and sample dispersion unit, a 3-way stopcock was installed through which a sample was transferred to the filtration unit. A sample reservoir on top of the filtration unit was designed with a volume of exactly 50.0 mL. The remaining suspension was still continuously circulating in the measurement device and thus controlled for particle concentration and size distribution. Up to fifteen loadings were done from one sample suspension on polycarbonate (Nuclepore) filters with a 47 mm diameter and 0.4 μm pore size. Each of the filters had been preconditioned in a clean room and weighed to obtain its tare weight. Filtration of sub-samples (50.0 mL) was performed with the help of a vacuum pump, which was strong enough to ensure that the particles were strongly bound to the filter. After filtration, the filters were dried at 50 °C and weighed to obtain filter mass loadings. The samples were put into plastic petri dishes and stored under the clean room conditions before dispatch. The stability of the sample loading was only assessed by weighing the filters during the period of storage. Stability under clean room conditions was confirmed.

The homogeneity of the material deposited on a filter was assessed by micro-beam XRF. Measurements were made across the central part of a filter and at the edge of the filter deposit. Parallel tracks of the measurements were 0.2 mm apart. XRF measurements of iron in the central part of the filter showed a variation of 3-4 % (including components due to sample inhomogeneity and instrumental imprecision) . For the measurements at the edge of the filter, a rapid decrease in the deposit thickness was apparent. The decrease was observed within 0.5 mm of the deposit edge. For this reason, when micro-beam techniques (micro-beam XRF, PIXE) are used the central part of the filter should be measured.

The loaded air filters and accompanying blanks were distributed to the participating laboratories with information about the mass loadings and instructions on handling the filters before the analysis and reporting the results.

Assigned Value and Target Standard Deviation

The consensus values established during the intercomparison survey on IAEA-NAT-3 candidate reference material, published in report [4], were used as the assigned values of the analytes, X_A. The results for 45 analytes were submitted and evaluated in this proficiency test: Al, As, Au, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Eu, Fe, Ga, Ge, Hf, Hg, I, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Sc, Si, Sm, Sr, Tb, Th, Ti, U, V, W, Yb, and Zn. For each

analyte a target value of the standard deviation has been assigned using a modified Horowitz function as proposed in the reference [5]:

$$H_A = \begin{cases} 0.22X_A & X_A < 1.2\cdot 10^{-7} \\ 0.02\left(X_A\right)^{0.8495} & 1.2\cdot 10^{-7} \le X_A \le 0.138 \\ 0.01\sqrt{X_A} & X_A > 0.138 \end{cases} \quad (1)$$

In Eqn. (1) the assigned value of analyte, X_A, is expressed as a mass fraction. The target value of the standard deviation, σ_A is related to H_A by a factor k:

$$\sigma_A = kH_A, \quad k = 0.5, 1.0, 1.5 \quad (2)$$

Depending on the value of the factor k the target value of the standard deviation is recognized as fit-for-purpose at three levels of uncertainty: k = 0.5 - appropriate for high precision analysis; k = 1.0 - appropriate for well established routine analysis; k = 1.5 - satisfactory for common analytical tasks. The relative value of the target standard deviation, *RSD*, expressed in per cent, is defined as follows:

$$RSD = \frac{\sigma_A}{X_A}\cdot 100\% \quad (3)$$

The relative value of the target standard deviation as a function of the assigned mass fraction of the analyte, X_A, is presented in Fig. 1.

***Z*-Scores and *U*-Scores.**

The reported concentrations of analytes were compared with the assigned values using the *z*-score analysis. For every result a *z*-score was calculated:

$$z = \frac{x - X_A}{\sigma_A} \quad (4)$$

The term '*x*' denotes the reported mass fraction of analyte. Defined by different fit-for-purpose ranges of the target standard deviation three different values of *z*-scores were calculated by combining Eqns. (2) and (4). Assuming that appropriate values for X_A and σ_A have been used and that the underlying distribution of analytical errors is normal, apart from outliers, in a well-behaved analytical system *z*-scores would be expected to fall outside the range $-2 \le z \le 2$ in about 4.6% of instances, and outside the range $-3 < z < 3$ only in about 0.3%. Therefore, based on the z-scores the following decision limits were established:

$$\begin{aligned} |z| &\le 2 && \text{- a satisfactory result,} \\ 2 < |z| &< 3 && \text{- the result is considered questionable,} \\ |z| &\ge 3 && \text{- the result is considered unsatisfactory.} \end{aligned} \quad (5)$$

The advice to the laboratory is that falling for the fit-for-purpose range, selected by the laboratory, any *z*-score for an element outside the range $-2 \le z \le 2$ should be examined by the

analyst and all steps of the analytical procedure verified to identify the source(s) of the analytical bias.

For every participant the rescaled sum of *z*-scores, *RSZ*, as well as the sum of squared *z*-scores, *SSZ*, were calculated as defined by the following equations:

$$RSZ = \frac{\sum_{i=1}^{L} z_i}{\sqrt{L}} \tag{6}$$

$$SSZ = \sum_{i=1}^{L} (z_i)^2 \tag{7}$$

The symbol '*L*' denotes the number of results provided by the laboratory/participant for all the analytes determined. The summing up in Eqns. (6) and (7) takes into account all *z*-scores for all analytes reported by participant. The *RSZ* can be interpreted as a standardized normally distributed variable, with expected value equal to zero and unit variance. It is sensitive in detecting a small consistent bias in an analytical system, however, it is not sensitive in cases where there are even big errors but having opposite signs. The *SSZ* takes no account of the signs because it depends on the squared *z*-scores. It has a chi-squared (χ^2) distribution with *L* degrees of freedom. The *SSZ* can be regarded as complementary to *RSZ*, which means that if *RSZ* is well within the range $-3 < RSZ < 3$ and if at the same time value of *SSZ* is above the $\chi^2_{critical}$ value the overall performance of the laboratory requires improvement.

The reported results were accompanied by the standard uncertainty estimate made by the participant. The values were used to calculate *u*-scores:

$$u = \frac{|x - X_A|}{\sqrt{(\sigma_A)^2 + (\sigma_x)^2}} \tag{8}$$

The symbol 'σ_x' denotes the standard uncertainty of the submitted result *x*. If the assumptions about X_A and σ_A and about the normality of the underlying distributions are correct, and the laboratory estimate of σ_x takes into account all the significant sources of uncertainty, the *u*-scores would have a truncated normal distribution with unit variance. In a well-behaved analytical system only 0.1% of *u*-scores would fall outside the range $u < 3.29$. Therefore, the following decision limits for the *u*-scores were established:

$1.64 \geq u$ - reported result does not differ from the assigned value,
$1.64 < u \leq 1.95$ - reported result probably does not differ from the assigned value,
$1.95 < u \leq 2.58$ - it is not clear whether the reported and assigned values differ, (9)
$2.58 < u \leq 3.29$ - reported result is probably different from the assigned value,
$3.29 < u$ - reported result differs from the assigned value.

The *u*-scores are especially useful for deciding whether the laboratory fit-for-purpose criteria are fulfilled. By comparing Eqn. (4) and Eqn. (8) one can immediately notice that for corresponding values of *u*-score and *z*-score the following inequality is always fulfilled:

$$u < z \tag{10}$$

It implies that if the *u*-score falls outside the range $u < 3.29$ also the decision limit for the corresponding *z*-score is triggered and the laboratory has to check the analytical procedure as well as review the uncertainty budget estimation. If *u*-score stays within the range u < 1.64 but at the same time the *z*-score decision limit is triggered ($|z| > 3$) the laboratory should re-evaluate its fit-for-purpose status for that particular analyte.

Consensus Values

To examine the overall performance of the NAT applied by the participants of the proficiency test the submitted results have been also statistically processed and the consensus values were calculated. The results were tested for the presence of outliers using a set of seven outlier rejection tests:

description of symbols:

$x_1 < ... < x_n$ - set of analytical results,
$\bar{x}$ - mean value, (11)
s - standard deviation,

1. Coefficient of kurtosis [6], number of results: $5 \le n \le 100$, two-sided test, confidence level = 0.95:

$$b_2 = \frac{n\sum_{i=1}^{n}(\bar{x} - x_i)^4}{\left[\sum_{i=1}^{n}(\bar{x} - x_i)^2\right]^2} \quad (12)$$

- if b_2 > critical value then reject the result that is at the furthest distance from the mean, decrease *n*, repeat the procedure until $b_2 \le$ critical value.

2. Coefficient of skewness [6], number of results, $5 \le n \le 60$, one-sided test, confidence level = 0.95:

$$\sqrt{b_1} = \frac{\sqrt{n}\sum_{i=1}^{n}(x_i - \bar{x})^3}{\left[\sum_{i=1}^{n}(x_i - \bar{x})^2\right]^{3/2}} \quad (13)$$

- if $\left|\sqrt{b_1}\right|$ > critical value then: if $\sqrt{b_1}$ is positive then reject x_n, otherwise reject x_1, decrease *n*, repeat the procedure until $\left|\sqrt{b_1}\right| \le$ critical value.

3. Veglia's test [7, 8], number of results: $4 \le n \le \infty$, two-sided test, confidence level = 0.95:

$$h = \sqrt{\frac{n}{n-1}}\frac{|x_k - \bar{x}_{n-1}|}{s_{n-1}} \quad (14)$$

where:
x_k, examined value, the result at the furthest distance from the mean
$\bar{x}_{n-1}$, the mean value of the population of the results with the examined result excluded
s_{n-1}, the standard deviation of the population of the results with the examined result excluded

- if $h >$ critical value then reject x_k otherwise temporarily exclude the x_k from the population of results and proceed with testing the next outlier candidate, if the following value of $h >$ critical value then reject both results, decrease n respectively, repeat the procedure until $h \leq$ critical value.

4. Dixon's test [9], number of results: $3 \leq n \leq 25$, two-sided test, confidence level = 0.95:

- if x_1 is at the furthest distance from the mean value, then calculate:

$$r = \begin{cases} (x_2 - x_1)/(x_n - x_1), & 3 \leq n \leq 7 \\ (x_2 - x_1)/(x_{n-1} - x_1), & 8 \leq n \leq 10 \\ (x_3 - x_1)/(x_{n-1} - x_1), & 11 \leq n \leq 13 \\ (x_3 - x_1)/(x_{n-2} - x_1), & 14 \leq n \leq 25 \end{cases} \tag{15a}$$

- if x_n is at the furthest distance from the mean value then calculate:

$$r = \begin{cases} (x_n - x_{n-1})/(x_n - x_1), & 3 \leq n \leq 7 \\ (x_n - x_{n-1})/(x_n - x_2), & 8 \leq n \leq 10 \\ (x_n - x_{n-2})/(x_n - x_2), & 11 \leq n \leq 13 \\ (x_n - x_{n-2})/(x_n - x_3), & 14 \leq n \leq 25 \end{cases} \tag{15b}$$

- if $r >$ critical value then reject the tested result, decrease n, repeat the procedure until $r \leq$ critical value.

5. Outlier rejection test proposed in [6], number of results: $4 \leq n \leq 100$, two-sided test, confidence level = 0.95:

$$w/s = (x_n - x_1)/s \tag{16}$$

- if $w/s >$ critical value then: if $x_n - \bar{x} = \bar{x} - x_1$, reject both x_1 and x_n, otherwise reject x_k ($x_k = x_1$ *or* $x_k = x_n$), the result that is at the furthest distance from the mean, for the remaining population of results ($n` = n - 1$) calculate: $T_k = |\bar{x}' - x_k| / s'$, where: $\bar{x}'$ is the mean value and s' is the standard deviation of the population of the results excluding the rejected value x_k, if $T_k >$ critical value then reject also the second extreme result, decrease n respectively, repeat the procedure until w/s ≤ critical value.

6. Outlier rejection test proposed in [10], number of results: $3 \leq n < \infty$, two-sided test, confidence level = 0.95:

$$B_4 = \left| x_k - \bar{x} \right| / s \quad (17)$$

where:

x_k , examined value

- if B_4 > critical value then reject the tested result, repeat the procedure until $B_4 \leq$ critical value.

7. Outlier rejection test proposed in [11], number of results: $3 \leq n \leq 100$, two-sided test, confidence level = 0.95:

$$S_k^2 / S = \frac{\sum_{i=1, i \neq k}^{n} (x_i - \bar{x}')^2}{\sum_{i=1, i \neq k}^{n} (x_i - \bar{x})^2}, \quad k = 1 \; or \; k = n \quad (18)$$

where:

x_k , examined value, the result at the furthest distance from the mean

$\bar{x}'$, the mean value of the population of the results with the examined result x_k excluded

- if $S_k^2 / S >$ critical value then reject x_k , decrease *n*, repeat the procedure until $S_k^2 / S \leq$ critical value.

The results which passed the outlier rejection procedures were used to calculate the consensus mean value of analyte, X_C, and corresponding consensus value of its standard deviation, σ_C:

$$X_C = \frac{\sum_{i=1}^{m} x_i}{m} \quad (19)$$

and

$$\sigma_C = \sqrt{\frac{\sum_{i=1}^{m} (x_i - X_C)^2}{m(m-1)}} \quad (20)$$

The term *m* denotes the number of reported values for a given analyte excluding the outliers rejected by at least one of the outlier rejections tests. The summing up in Eqn. (19) and (20) takes into account only the results which passed all the outlier rejection tests. The obtained consensus values were compared with the assigned values of analytes.

RESULTS

The urban dust material loaded on polycarbonate filters was distributed to 24 laboratories applying NAT technique for elemental analysis. Out of the 24 laboratories 12 have provided the required analytical results. The list of the participating laboratories is presented

in Table 1. Four different analytical techniques have been used by the participants of the proficiency test. The techniques and technique codes are listed in Table 2. The participants provided 175 analytical results for 45 analytes. All submitted results have been evaluated. In Table 3 a summary of the assigned analyte values, the target values of standard deviation, as well as the consensus values are shown. The consensus values were calculated using Eqns.(19) and (20) based on 146 reported analytical results after excluding 29 results classified as outliers. The correlation between the assigned and the consensus values is shown in Fig. 2. As can be noticed there are quite a few elements for which there is significant disagreement between the assigned and the consensus values. These elements include "difficult" ones such as Hg, I, Cd, Cl, Co and/or the elements determined by only one or two laboratories: W, Ga, Ge, S. The disagreement is also observed for a few other elements including Br, Cu, Ni, and Zn, which in the case of bulk analysis (not on a filter media) do not pose analytical problems The remaining results correlate well with the assigned values of analytes. In Table 4 all the submitted results are listed together with *z*-scores and *u*-scores calculated for the three different fit-for-purpose ranges, as defined in Eqn. (2). In Figs. 3 and 4 the distributions of the proficiency test results are shown. In Fig. 3 the distributions of results for the analytes for which at least 6 results passed the outlier rejection tests are shown. Due to rather low number of results, these graphs could only be used as indicators of the trends observed in the reported data. All the populations of results have passed a normality test (Kolmogorov-Smirnov). In Fig. 4 the bar chart distributions of the *z*-scores are presented for analytes for which at least 5 results passed the outlier detection procedures. The results are sorted in ascending order versus laboratory code and they are accompanied by technique codes marked on a linked upper *X*-axis. The decision levels $|z| < 2$ for different fit-for-purpose ranges have also been marked on the graphs. For every participating laboratory its overall performance is presented in Fig. 5. The graphs presented in this figure relate all the *u*-scores and *z*-scores calculated for a given laboratory. The decision limits marked with black lines ($|z| < 3$, $u < 3.29$) divide the plot area in four quadrants. Due to inequality (10) all the points lay always below the line $u = z$. The smaller the laboratory estimated uncertainty is the closer the related point lays to the $u = z$ line. The better performing laboratories would have more points located in the lower-left quadrant of the plot. If there are many points located in the upper-right quadrant it suggests that these results do not fall in the defined fit-for-purpose ranges and that the laboratory provided too "optimistic" uncertainty estimate which requires some care and revision. The participants are advised to examine in detail their results presented in Table 4, Figs. 4 and 5 in order to better define their fit-for-purpose status as well to identify the analytes or analyte groups requiring improvement in the analytical procedures.

The partitioning of the results between different analytical techniques is presented in Fig.6. As can be noticed the majority of the determinations were carried out by NAA (50.3%) and EDXRF (32.9%) techniques. The rest of the submitted results was obtained by PIXE (11.0%), and AAS (5.8%).

It has to be emphasized that to really benefit from the proficiency testing a regular participation in the scheme is required.

ACKNOWLEDGMENT

The organizers of the proficiency test are grateful to the Colleagues from the Chemistry Unit, IAEA Seibersdorf Laboratories for provision of the loaded air filters which were used in the exercise. We also thank the participants for taking part in the proficiency test and for providing the additional information on the analytical process.

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APPENDIX I

Tables 1-5

Table 1. The laboratories participating in the proficiency test exercise.

Analyst Name	Institution	Country
Rita Plá	Técnicas Analíticas Nucleares (CAE), Comisión Nacional de Energía Atómica	**Argentina**
Eduardo Cortes Toro	Comisión Chilena de Energía Nuclear	**Chile**
Kresimir Sega	Environmental Hygiene Unit, Institute for Medical Research and Occupational Health	**Croatia**
Francisca Aldape de Flores	Instituto Nacional de Investigaciones Nucleares (ININ)	**Mexico**
Nikolla Civici	Institute of Nuclear Physics	**Albania**
Borut Smodis	Jozef Stefan Institute, Department of Environmental Sciences	**Slovenia**
Aneta Stefanovska	Ministry of Environment and Physical Planning	**The Former Yugoslav Republic of Macedonia**
A. G. Karydas, Ch. Zarkadas	NCSR Demokritos, Institute of Nuclear Physics	**Greece**
Flora L. Santos	Analytical Measurements Research Group, Philippine Nuclear Research Institute	**Philippines**
Alfonso Salazar	Universidad de Costa Rica	**Costa Rica**
Mirjana Radenkovic	Vinca Institute of Nuclear Science Radiation and Environmental Protection Laboratory	**Serbia**
Nilgün Çelebi	Çekmece Nuclear Research and Training Center	**Turkey**

Table 2. The coding, description and the abbreviated names of the analytical techniques used by participants of the proficiency test exercise.

Technique Code	Description	Abbreviation
1.0	Energy dispersive X-ray fluorescence spectrometry	EDXRF
4.0	Proton induced X-ray emission	PIXE
5.0	Neutron activation analysis	NAA
7.0	Atomic Absorption Spectrometry	AAS
7.1	Graphite furnace atomic absorption spectrometry	GFAAS
7.2	Flame atomic absorption spectrometry	FAAS
7.3	Hydride generation atomic absorption spectrometry	HGAAS
7.5	Cold vapor atomic absorption spectrometry	CVAAS

Table 3. The assigned analyte values adapted from [4], the target values of the standard deviations obtained by using modified Horowitz function, Eqn. (1), and the consensus values calculated as described in the report. For the analytes marked in bold the assigned values are based on results obtained by several analytical techniques, as stated in the IAEA/NAHRES-43 report [4]. The populations with at least 5 reported results were tested for normality by using Kolmogorov-Smirnov test, all examined populations passed the test.

Analyte symbol	Assigned value of the analyte, X_A	Target value of standard deviation, σ_A			Consensus value of the analyte, X_C	Consensus value of the standard deviation, σ_C	Number of results	Number of outliers
		$k = 0.5$	$k = 1.0$	$k = 1.5$				
				[g/kg]				
Al	34.1	0.57	1.2	1.7	30	11	5	0
Ca	27.96	0.48	0.96	1.44	23.72	0.95	8	2
Cl	1.426	0.039	0.077	0.12	2.36	0.13	4	1
Fe	48.3	0.76	1.6	2.3	50.1	2.3	9	2
K	9.79	0.20	0.40	0.60	9.02	0.14	7	4
Mg	10.83	0.22	0.43	0.65	13.892	0.042	2	0
Na	3.36	0.079	0.16	0.24	3.296	0.015	5	3
P	1.806	0.047	0.094	0.14	1.58	0.15	1	0
S	1.97	0.051	0.10	0.16	3.52	0.85	2	0
Si	90.2	1.3	2.6	3.9	114.1	1.2	3	1
Ti	2.60	0.064	0.13	0.20	2.60	0.13	6	2
Zn	3.98	0.092	0.19	0.28	1.741	0.066	10	3
				[mg/kg]				
As	23.0	1.2	2.3	3.5	24.3	1.6	4	0
Au	0.59	0.051	0.11	0.16	0.68	0.19	2	0
Ba	753	23	45	67	786	96	4	0
Br	60.0	2.6	5.2	7.8	202.9	6.2	6	3
Cd	3.00	0.21	0.41	0.61	26.1	7.0	2	0
Ce	33.6	1.6	3.2	4.8	36.63	0.65	3	0
Co	18.8	0.97	2.0	3.0	11.29	0.17	5	2
Cr	412	13	27	40	381	83	8	0
Cs	4.33	0.28	0.56	0.84	3.491	0.029	4	2
Cu	807	24	48	71	1378	168	9	1
Dy	2.27	0.16	0.33	0.49	1.90	0.14	1	0
Eu	0.73	0.06	0.13	0.19	0.750	0.020	2	0
Ga	18.7	0.97	2.0	2.9	12.37	0.83	1	0
Ge	15.0	0.8	1.6	2.4	40	20	1	0
Hf	3.48	0.24	0.47	0.70	4.07	0.15	3	0
Hg	1.67	0.13	0.25	0.38	26	12	3	0
I	4.10	0.27	0.53	0.80	12.7	1.9	1	0
La	21.9	1.1	2.2	3.3	22.2	2.8	3	0
Mn	558	18	35	52	542	88	10	0
Mo	65.0	2.8	5.6	8.4	46.7	2.3	1	0
Ni	243	8.5	17	26	122	25	8	0

Table 3 continued…

Analyte symbol	Assigned value of the analyte, X_A	Target value of standard deviation, σ_A			Consensus value of the analyte, X_C	Consensus value of the standard deviation, σ_C	Number of results	Number of outliers
		$k = 0.5$	$k = 1.0$	$k = 1.5$				
Pb	583	18	36	54	570	118	8	0
Rb	63.8	2.7	5.5	8.2	52.8	4.8	2	0
Sb	127.4	5.0	9.9	15	156.01	0.31	3	1
Sc	6.33	0.39	0.77	1.2	5.13	0.17	3	0
Sm	3.10	0.21	0.42	0.63	2.571	0.049	2	0
Sr	130	5	10	15	115	44	1	0
Tb	0.540	0.048	0.095	0.15	0.462	0.066	1	0
Th	5.26	0.33	0.66	0.99	4.97	0.11	3	0
U	4.46	0.29	0.57	0.86	3.27	0.18	1	0
V	94.5	3.9	7.7	12	97.2	1.7	4	1
W	7.47	0.45	0.89	1.4	12.20	0.50	1	0
Yb	2.01	0.15	0.29	0.44	1.49	0.34	2	0

Table 4. Summary of the reported results and the calculated *z*-scores and *u*-scores. The results rejected by the outliers rejection procedures were marked with '*' in the "Analyte concentration" column. In brackets, following the element symbol, the assigned values of element concentration and target standard deviation, for $k = 1$, are shown.

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
Al (34.1 ± 1.2) [g/kg]										
12	7.2	4.5	2.4	54.27	-52.22	-26.11	-17.41	11.84	11.02	9.97
11	7.1	7.92	0.64	8.12	-46.18	-23.09	-15.39	30.54	20.08	14.40
2	5.0	38.60	0.81	2.10	7.95	3.98	2.65	4.56	3.23	2.39
6	5.0	39.3	2.1	5.41	9.17	4.59	3.06	2.36	2.16	1.91
9	1.0	57.8	2.4	4.17	41.76	20.88	13.92	9.56	8.88	8.02
Ca (27.96 ± 0.96) [g/kg]										
10	1.0	8.90*	0.74	8.27	-39.79	-19.90	-13.26	21.70	15.78	11.80
5	1.0	20.8	2.0	9.77	-15.01	-7.51	-5.01	3.45	3.20	2.89
4	4.0	21.9	1.5	6.79	-12.62	-6.31	-4.21	3.87	3.42	2.92
9	1.0	22.65	0.63	2.78	-11.08	-5.54	-3.69	6.70	4.63	3.38
2	5.0	24.5	2.9	11.67	-7.22	-3.61	-2.41	1.19	1.15	1.08
8	1.0	25.9	1.2	4.63	-4.37	-2.18	-1.46	1.62	1.36	1.12
6	5.0	26.6	1.6	5.95	-2.85	-1.42	-0.95	0.82	0.74	0.64
12	7.2	43.18*	0.74	1.72	31.78	15.89	10.59	17.24	12.56	9.41
Cl (1.426 ± 0.077) [g/kg]										
2	5.0	1.17*	0.25	21.37	-6.70	-3.35	-2.23	1.01	0.98	0.93
9	1.0	2.14	0.11	4.93	18.56	9.28	6.19	6.34	5.46	4.56
4	4.0	2.35	0.16	7.00	24.06	12.03	8.02	5.46	5.08	4.59
6	5.0	2.589	0.099	3.82	30.41	15.21	10.14	10.96	9.30	7.68
Fe (48.3 ± 1.6) [g/kg]										
10	1.0	17.6*	1.4	7.69	-40.29	-20.15	-13.43	19.77	15.07	11.56
1	5.0	41.70	0.73	1.75	-8.68	-4.34	-2.89	6.27	3.91	2.76
2	5.0	44.7	1.2	2.60	-4.74	-2.37	-1.58	2.60	1.89	1.41
6	5.0	46.4	1.6	3.52	-2.49	-1.25	-0.83	1.05	0.85	0.68
5	1.0	50.2	5.1	10.11	2.46	1.23	0.82	0.37	0.35	0.34
4	4.0	55.5	3.8	6.82	9.38	4.69	3.13	1.85	1.75	1.62
12	7.2	55.50	0.91	1.64	9.42	4.71	3.14	6.06	4.05	2.92
9	1.0	56.8	1.5	2.68	11.09	5.54	3.70	4.96	3.92	3.08
11	7.1	89.0*	1.8	2.00	53.41	26.71	17.80	21.04	17.38	14.05
K (9.79 ± 0.40) [g/kg]										
10	1.0	1.54*	0.49	31.97	-42.01	-21.00	-14.00	15.57	13.10	10.75
12	7.2	2.4*	3.9	163.9	-37.67	-18.83	-12.56	1.88	1.88	1.87
6	5.0	8.77	0.33	3.76	-5.19	-2.60	-1.73	2.66	1.99	1.51
4	4.0	9.07	0.62	6.82	-3.67	-1.83	-1.22	1.11	0.98	0.84
5	1.0	9.2	1.7	18.78	-2.86	-1.43	-0.95	0.32	0.32	0.31
9	1.0	10.19*	0.42	4.17	2.04	1.02	0.68	0.86	0.69	0.55
8	1.0	10.51*	0.62	5.93	3.64	1.82	1.21	1.10	0.97	0.83

Table 4 continued…

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
Mg (10.83 ± 0.43) [g/kg]										
6	5.0	13.9	1.2	8.33	14.12	7.06	4.71	2.57	2.46	2.29
9	1.0	13.93	0.97	6.94	14.51	7.26	4.84	3.13	2.94	2.67
12	7.2	15.57*	0.17	1.06	22.17	11.09	7.39	17.56	10.34	7.16
Na (3.36 ± 0.16) [g/kg]										
2	5.0	2.88*	0.11	3.82	-6.09	-3.05	-2.03	3.56	2.50	1.84
6	5.0	3.28	0.12	3.52	-1.03	-0.51	-0.34	0.58	0.42	0.31
1	5.0	3.310	0.090	2.72	-0.66	-0.33	-0.22	0.44	0.29	0.21
9	1.0	5.0*	1.1	22.08	20.76	10.38	6.92	1.48	1.47	1.46
12	7.2	8.7*	8.9	101.6	67.98	33.99	22.66	0.61	0.61	0.61
P (1.806 ± 0.094) [g/kg]										
9	1.0	1.58	0.15	9.40	-4.92	-2.46	-1.64	1.48	1.31	1.13
S (1.97 ± 0.10) [g/kg]										
4	4.0	2.67	0.20	7.36	13.90	6.95	4.64	3.45	3.17	2.82
9	1.0	4.36	0.20	4.50	47.43	23.71	15.81	11.78	10.82	9.64
Si (90.2 ± 2.6) [g/kg]										
4	4.0	68.1*	6.3	9.28	-17.10	-8.55	-5.70	3.44	3.25	2.99
8	1.0	113	12	10.65	17.55	8.78	5.85	1.88	1.85	1.80
9	1.0	115.2	4.8	4.16	19.31	9.65	6.44	5.04	4.59	4.05
Ti (2.60 ± 0.13) [g/kg]										
10	1.0	1.21*	0.11	8.68	-21.80	-10.90	-7.27	11.29	8.40	6.37
2	5.0	2.35	0.23	9.79	-3.88	-1.94	-1.29	1.03	0.94	0.83
4	4.0	2.43	0.17	6.84	-2.57	-1.28	-0.86	0.92	0.78	0.65
9	1.0	2.740	0.092	3.38	2.24	1.12	0.75	1.27	0.91	0.67
5	1.0	2.88	0.32	11.04	4.52	2.26	1.51	0.89	0.84	0.77
8	1.0	3.61*	0.22	6.15	15.92	7.96	5.31	4.38	3.96	3.46
Zn (3.98 ± 0.19) [g/kg]										
10	1.0	0.597*	0.045	7.56	-37.00	-18.50	-12.33	33.18	17.96	12.17
2	5.0	1.500	0.083	5.53	-27.13	-13.57	-9.04	20.09	12.35	8.66
1	5.0	1.581	0.034	2.15	-26.25	-13.12	-8.75	24.60	12.90	8.68
6	5.0	1.698	0.066	3.88	-24.96	-12.48	-8.32	20.25	11.74	8.09
5	1.0	1.70	0.22	12.75	-24.93	-12.46	-8.31	9.68	8.03	6.52
4	4.0	1.82	0.13	6.95	-23.66	-11.83	-7.89	13.88	9.74	7.17
8	1.0	1.89	0.10	5.52	-22.92	-11.46	-7.64	15.13	9.96	7.14
9	1.0	2.003	0.062	3.11	-21.63	-10.82	-7.21	17.89	10.24	7.03
12	7.2	3.256*	0.045	1.38	-7.93	-3.97	-2.64	7.12	3.85	2.61
11	7.1	11.3*	1.1	9.70	79.94	39.97	26.65	6.65	6.59	6.48

Table 4 continued…

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
As (23.0 ± 2.3) [mg/kg]										
6	5.0	20.28	0.82	4.07	-2.38	-1.19	-0.79	1.94	1.12	0.77
1	5.0	23.5	4.7	20.00	0.42	0.21	0.14	0.10	0.09	0.08
2	5.0	26.0	2.1	8.08	2.60	1.30	0.87	1.25	0.96	0.74
7	7.0	27.30193	-	-	3.73	1.87	1.24	3.73	1.87	1.24
Au (0.59 ± 0.11) [mg/kg]										
6	5.0	0.495	0.017	3.33	-1.87	-0.93	-0.62	1.78	0.92	0.62
2	5.0	0.86	0.19	21.51	5.29	2.64	1.76	1.41	1.28	1.12
Ba (753 ± 45) [mg/kg]										
6	5.0	587	41	7.02	-7.46	-3.73	-2.49	3.54	2.74	2.12
2	5.0	740	70	9.46	-0.58	-0.29	-0.19	0.17	0.15	0.13
1	5.0	770	260	33.77	0.78	0.39	0.26	0.07	0.07	0.06
9	1.0	1046	118	11.31	13.19	6.59	4.40	2.43	2.32	2.16
Br (60.0 ± 5.2) [mg/kg]										
10	1.0	60*	15	25.00	-0.11	-0.06	-0.04	0.02	0.02	0.02
8	1.0	88*	15	16.70	10.69	5.35	3.56	1.86	1.78	1.67
9	1.0	191	30	15.42	50.75	25.38	16.92	4.44	4.39	4.31
4	4.0	205	29	14.18	55.78	27.89	18.59	4.96	4.91	4.81
6	5.0	212.7	8.2	3.88	58.94	29.47	19.65	17.67	15.68	13.48
1	5.0	246.0*	2.2	0.89	71.79	35.90	23.93	54.73	33.04	23.03
Cd (3.00 ± 0.41) [mg/kg]										
3	7.1	19.13	0.56	2.91	79.46	39.73	26.49	27.26	23.44	19.56
12	7.1	32.99	0.41	1.23	147.7	73.84	49.23	65.92	52.15	40.93
Ce (33.6 ± 3.2) [mg/kg]										
1	5.0	35.4	2.0	5.65	1.12	0.56	0.37	0.70	0.47	0.34
2	5.0	36.9	3.5	9.49	2.07	1.03	0.69	0.85	0.69	0.56
6	5.0	37.6	1.5	3.95	2.51	1.25	0.84	1.83	1.14	0.80
Co (18.8 ± 2.0)[mg/kg]										
2	5.0	11.06	0.72	6.51	-8.01	-4.01	-2.67	6.43	3.76	2.59
6	5.0	11.21	0.49	4.41	-7.86	-3.93	-2.62	6.99	3.81	2.58
1	5.0	11.60	0.67	5.78	-7.46	-3.73	-2.49	6.13	3.52	2.42
12	7.1	105.5*	5.2	4.89	89.58	44.79	29.86	16.50	15.72	14.63
4	4.0	362*	60	16.54	354.4	177.2	118.1	5.73	5.73	5.72

Table 4 continued…

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
				Cr (412 ± 27) [mg/kg]						
11	7.1	58.8	3.9	6.64	-26.53	-13.26	-8.84	25.46	13.12	8.80
10	1.0	134	15	11.17	-20.87	-10.44	-6.96	13.87	9.10	6.52
2	5.0	277.3	4.1	1.48	-10.11	-5.05	-3.37	9.66	5.00	3.35
4	4.0	425	30	7.03	1.01	0.50	0.34	0.41	0.33	0.27
9	1.0	427	30	6.97	1.15	0.57	0.38	0.47	0.38	0.31
1	5.0	442	14	3.17	2.26	1.13	0.75	1.56	1.00	0.71
6	5.0	462	16	3.57	3.74	1.87	1.25	2.35	1.59	1.15
8	1.0	821	63	7.72	30.76	15.38	10.25	6.32	5.96	5.47
				Cs (4.33 ± 0.56) [mg/kg]						
6	5.0	3.46	0.33	9.52	-3.13	-1.56	-1.04	2.02	1.35	0.97
2	5.0	3.52	0.53	15.06	-2.92	-1.46	-0.97	1.36	1.06	0.82
1	5.0	4.39*	0.65	14.81	0.21	0.10	0.07	0.08	0.07	0.05
12	7.2	5111*	169	3.31	18380	9188	6125	30.1	30.1	30.1
				Cu (807 ± 48) [mg/kg]						
10	1.0	462	30	6.53	-14.63	-7.31	-4.88	9.00	6.16	4.48
6	5.0	1167	106	9.04	15.31	7.66	5.10	3.34	3.12	2.84
5	1.0	1269	217	17.07	19.63	9.81	6.54	2.12	2.09	2.03
7	7.0	1290.15	-	-	20.52	10.26	6.84	20.52	10.26	6.84
4	4.0	1327	92	6.97	22.09	11.05	7.36	5.45	5.02	4.47
2	5.0	1730	130	7.51	39.19	19.59	13.06	6.99	6.68	6.24
9	1.0	1797	48	2.65	42.03	21.01	14.01	18.62	14.77	11.61
12	7.1	1982	23	1.18	49.88	24.94	16.63	35.33	22.32	15.78
11	7.1	3166*	127	4.01	100.1	50.06	33.38	18.27	17.42	16.23
				Dy (2.27 ± 0.33) [mg/kg]						
6	5.0	1.90	0.14	6.96	-2.33	-1.17	-0.78	1.80	1.08	0.75
				Eu (0.73 ± 0.13) [mg/kg]						
2	5.0	0.73	0.13	17.81	0.07	0.03	0.02	0.03	0.02	0.02
1	5.0	0.77	0.22	28.57	0.72	0.36	0.24	0.19	0.18	0.15
				Ga (18.7 ± 2.0) [mg/kg]						
6	5.0	12.37	0.82	6.67	-6.60	-3.30	-2.20	5.02	3.04	2.12
				Ge (15.0 ± 1.6) [mg/kg]						
4	4.0	40	20	50.21	30.94	15.47	10.31	1.24	1.24	1.23
				Hf (3.48 ± 0.47) [mg/kg]						
1	5.0	3.89	0.48	12.34	1.76	0.88	0.59	0.76	0.61	0.48
6	5.0	3.96	0.16	4.17	2.05	1.03	0.68	1.67	0.97	0.67
2	5.0	4.37	0.57	13.04	3.84	1.92	1.28	1.44	1.21	0.99

Table 4 continued…

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
				Hg (1.7 ± 0.25) [mg/kg]						
6	5.0	9.23	0.49	5.36	61.25	30.62	20.42	14.84	13.68	12.24
2	5.0	19.5	2.0	10.26	144.4	72.18	48.12	8.90	8.85	8.77
7	7.5	48.17987	-	-	376.5	188.3	125.5	376.5	188.3	125.5
				I (4.10 ± 0.53) [mg/kg]						
6	5.0	12.7	1.8	14.29	32.41	16.21	10.80	4.69	4.55	4.34
				La (21.9 ± 2.2) [mg/kg]						
6	5.0	18.47	0.66	3.57	-3.08	-1.54	-1.03	2.64	1.48	1.01
2	5.0	20.7	2.2	10.63	-1.05	-0.52	-0.35	0.47	0.37	0.29
1	5.0	27.5	1.0	3.64	5.14	2.57	1.71	3.80	2.34	1.64
				Mn (558 ± 35) [mg/kg]						
12	7.1	11	12	101.5	-31.73	-15.87	-10.58	26.36	15.04	10.32
10	1.0	239	30	12.52	-18.53	-9.26	-6.18	9.25	7.00	5.35
7	7.0	422.9122	-	-	-7.86	-3.93	-2.62	7.86	3.93	2.62
11	7.1	469.7	5.6	1.20	-5.15	-2.57	-1.72	4.89	2.54	1.71
6	5.0	554	20	3.57	-0.26	-0.13	-0.09	0.17	0.11	0.08
2	5.0	581	11	1.89	1.31	0.65	0.44	1.10	0.62	0.43
4	4.0	683	47	6.95	7.22	3.61	2.41	2.47	2.12	1.77
9	1.0	692	30	4.37	7.76	3.88	2.59	3.84	2.92	2.23
5	1.0	779	144	18.55	12.78	6.39	4.26	1.52	1.48	1.44
8	1.0	991	67	6.71	25.08	12.54	8.36	6.30	5.77	5.13
				Mo (65.0 ± 5.6) [mg/kg]						
6	5.0	46.7	2.3	4.95	-6.61	-3.31	-2.20	5.08	3.05	2.12
				Ni (243 ± 17) [mg/kg]						
12	7.1	6	18	329.1	-27.92	-13.96	-9.31	11.71	9.47	7.55
10	1.0	45	15	33.38	-23.32	-11.66	-7.77	11.54	8.76	6.71
11	7.1	117.5	6.2	5.29	-14.75	-7.38	-4.92	11.90	6.93	4.78
7	7.0	117.773	-	-	-14.72	-7.36	-4.91	14.72	7.36	4.91
4	4.0	139	13	9.17	-12.22	-6.11	-4.07	6.77	4.89	3.64
5	1.0	144	58	40.01	-11.61	-5.81	-3.87	1.69	1.64	1.57
9	1.0	191	15	7.76	-6.05	-3.03	-2.02	3.01	2.28	1.74
8	1.0	216	19	8.84	-3.13	-1.57	-1.04	1.27	1.04	0.84

Table 4 continued…

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
Pb (583 ± 36) [mg/kg]										
12	7.1	8.8	4.0	44.81	-32.11	-16.05	-10.70	31.35	15.96	10.67
10	1.0	239	15	6.32	-19.25	-9.62	-6.42	14.71	8.87	6.18
7	7.0	438.9722	-	-	-8.07	-4.04	-2.69	8.07	4.04	2.69
8	1.0	568	54	9.56	-0.83	-0.42	-0.28	0.26	0.23	0.19
3	7.1	695	11	1.65	6.25	3.12	2.08	5.26	2.97	2.04
5	1.0	721	44	6.08	7.70	3.85	2.57	2.91	2.43	1.99
4	4.0	872	70	7.98	16.12	8.06	5.37	4.02	3.69	3.28
9	1.0	1016	74	7.31	24.20	12.10	8.07	5.66	5.25	4.72
Rb (63.8 ± 5.5) [mg/kg]										
2	5.0	48.1	6.0	12.47	-5.76	-2.88	-1.92	2.39	1.94	1.55
6	5.0	57.5	4.9	8.60	-2.31	-1.15	-0.77	1.11	0.85	0.66
Sb (127.4 ± 9.9) [mg/kg]										
2	5.0	155.7	7.0	4.50	5.76	2.88	1.92	3.31	2.35	1.74
6	5.0	156.3	5.6	3.59	5.89	2.94	1.96	3.88	2.56	1.83
1	5.0	191.9*	1.3	0.68	13.13	6.57	4.38	12.69	6.51	4.36
Sc (6.33 ± 0.77) [mg/kg]										
1	5.0	4.893	0.074	1.51	-3.74	-1.87	-1.25	3.67	1.86	1.24
2	5.0	5.05	0.58	11.49	-3.33	-1.67	-1.11	1.84	1.33	0.99
6	5.0	5.44	0.16	3.03	-2.31	-1.16	-0.77	2.12	1.13	0.76
Sm (3.10 ± 0.42) [mg/kg]										
6	5.0	2.523	0.099	3.92	-2.76	-1.38	-0.92	2.50	1.34	0.91
2	5.0	2.62	0.34	12.98	-2.30	-1.15	-0.77	1.20	0.89	0.67
Sr (130 ± 10) [mg/kg]										
5	1.0	115	44	37.51	-2.96	-1.48	-0.99	0.34	0.33	0.32
Tb (0.540 ± 0.095) [mg/kg]										
6	5.0	0.462	0.066	14.29	-1.65	-0.83	-0.55	0.96	0.68	0.50
Th (5.26 ± 0.66) [mg/kg]										
1	5.0	4.77	0.32	6.71	-1.50	-0.75	-0.50	1.07	0.67	0.48
2	5.0	5.02	0.60	11.95	-0.74	-0.37	-0.25	0.35	0.27	0.21
6	5.0	5.11	0.20	3.87	-0.46	-0.23	-0.15	0.39	0.22	0.15
U (4.56 ± 0.57) [mg/kg]										
6	5.0	3.27	0.18	5.56	-4.19	-2.09	-1.40	3.53	2.00	1.37

Table 4 continued…

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
V (94.5 ± 7.7) [mg/kg]										
4	4.0	94	10	10.73	0.00	0.00	0.00	0.00	0.00	0.00
6	5.0	96.8	4.1	4.26	0.60	0.30	0.20	0.41	0.26	0.19
2	5.0	100.3	4.7	4.69	1.52	0.76	0.51	0.96	0.65	0.47
9	1.0	324*	30	9.15	60.22	30.11	20.07	7.68	7.50	7.23
W (7.47 ± 0.89) [mg/kg]										
6	5.0	12.20	0.49	4.05	10.71	5.35	3.57	7.13	4.67	3.34
Yb (2.01 ± 0.29) [mg/kg]										
6	5.0	1.15	0.12	10.00	-5.90	-2.95	-1.97	4.61	2.74	1.90
1	5.0	1.82	0.68	37.36	-1.29	-0.65	-0.43	0.27	0.25	0.23

Table 5. The combined *z*-scores for the participating laboratories.

Lab Code	Number of analytes	Rescaled sum of scores (RSZ)			Sum of squared scores (SSZ)			Critical value
		$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$	χ^2
1	17	11.58	5.79	3.86	6202	1551	689	30.19
2	26	24.20	12.10	8.07	23660	5916	2629	41.92
3	2	60.60	30.30	20.20	6353	1588	706	7.38
4	17	112.30	56.15	37.43	132500	33120	14720	30.19
5	10	-3.25	-1.63	-1.09	1633	408	181	20.48
6	35	25.26	12.63	8.42	10870	2718	1208	53.20
7	6	151.10	75.55	50.37	142600	35640	15840	14.45
8	10	22.89	11.45	7.63	2819	705	313	20.48
9	20	74.53	37.27	24.84	14930	3731	1658	34.17
10	11	-83.70	-41.85	-27.90	8723	2181	969	21.92
11	7	53.25	26.63	17.75	22350	5587	2483	16.01
12	14	4972.00	2486.00	1657.00	337700000	84430000	37530000	26.12

APPENDIX II

Figures 1-6

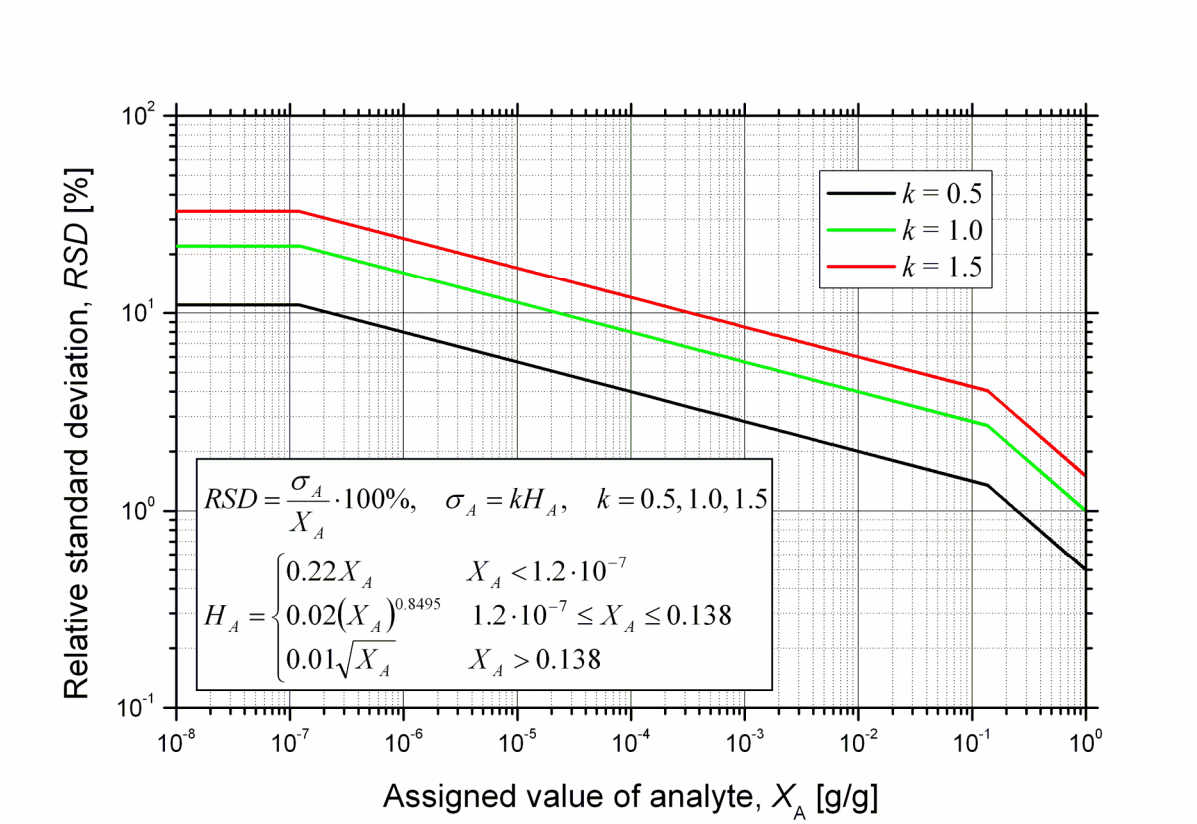


Fig. 1. Relative value of the target standard deviation, *RSD*, as a function of the assigned mass fraction of the analyte, X_A, calculated using a modified Horowitz function. The target value, σ_A, is related to H_A by a factor k and it is recognized as fit-for-purpose in three levels of uncertainty: ***k* = 0.5 - solid black line**, appropriate for high precision analysis; ***k* = 1.0 - solid green line**, appropriate for well established routine analysis; ***k* = 1.5 - solid red line**, satisfactory for common analytical tasks.

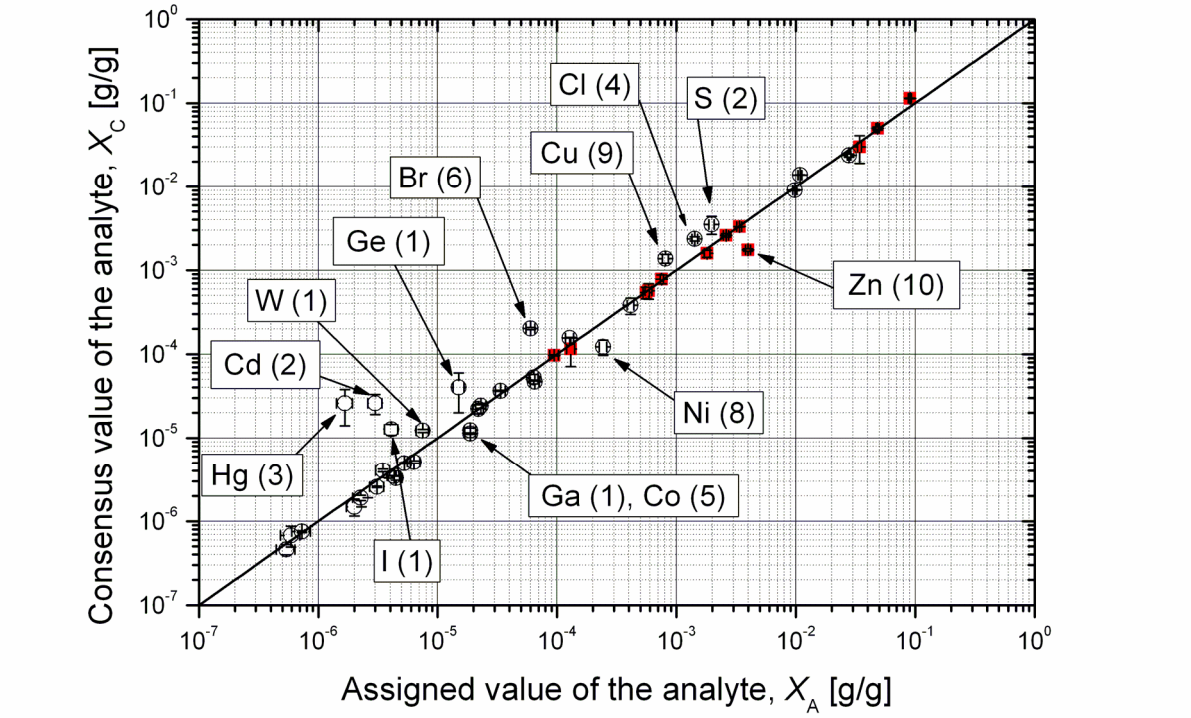


Fig. 2. Correlation between assigned values, X_A - the assigned values of elements concentrations taken from the IAEA/NAHRES-43 report [4], and consensus values of analytes, X_C – calculated based on the submitted results. Solid red squares correspond to elements the assigned values of which were based on results from several analytical techniques. Hollow black circles correspond to elements the assigned values of which were based on results from single analytical technique. The analytes for which significant disagreement between the assigned and consensus values was observed are marked on the graph (in brackets the number of reported results is given). The uncertainties of the assigned values shown on the graph were calculated according to Eqn. (2) with $k = 1$. The uncertainties of the consensus values were calculated using Eqn.(20), except for the results reported by single laboratory, in such a case the laboratory estimate of the uncertainty is shown.

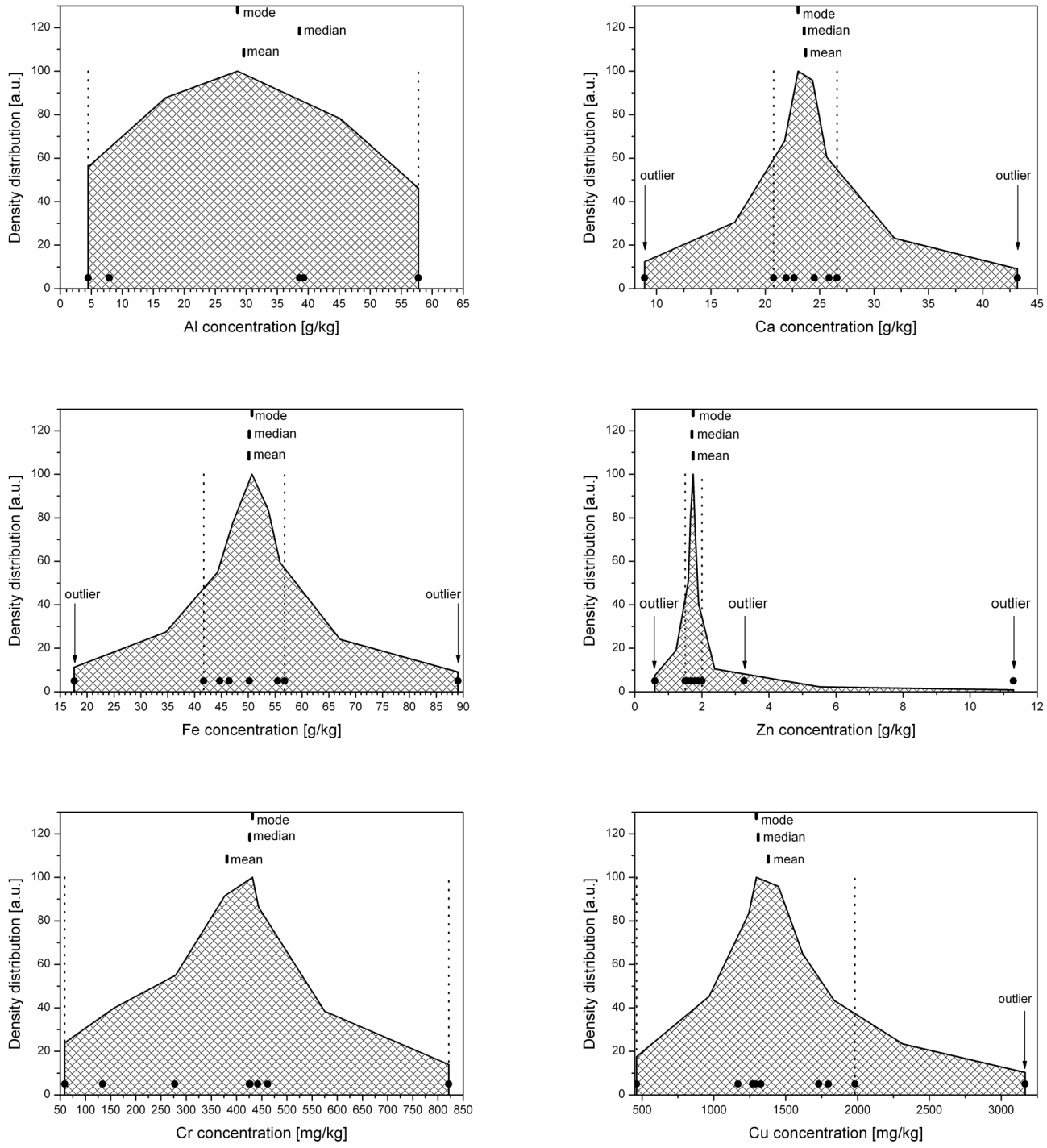
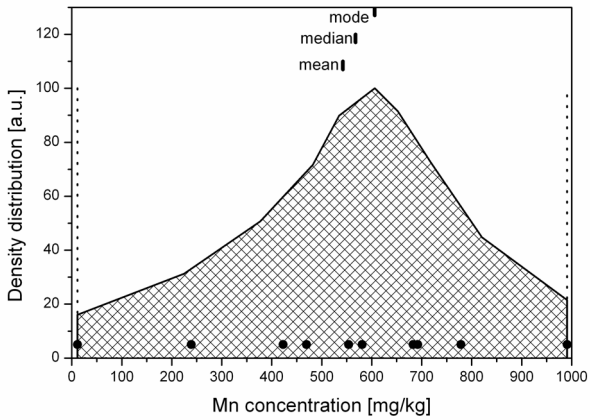
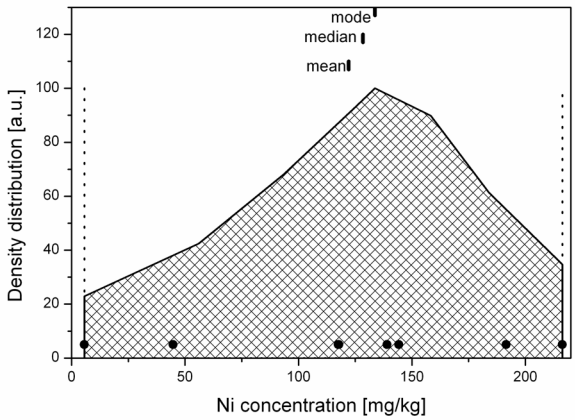
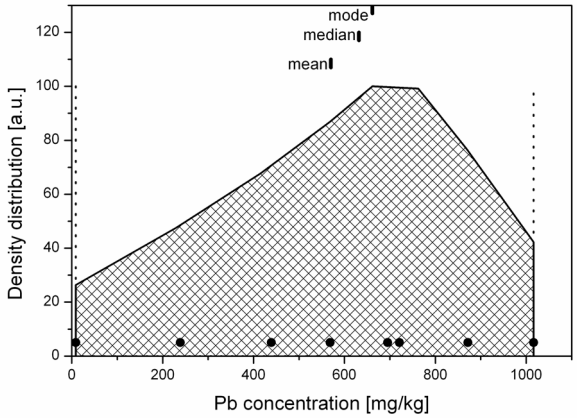


Fig. 3. The density distributions functions for the analytes for which at least 5 results passed the outlier rejection tests. The individual results are marked with filled circles. The dotted lines show the range of accepted results – these results were used to calculate the consensus values. The outliers marked with arrows. Also marked are the estimated parameters of the distributions (after outlier removal, if present): the mode, median, and the mean value.

Fig. 3 continued…







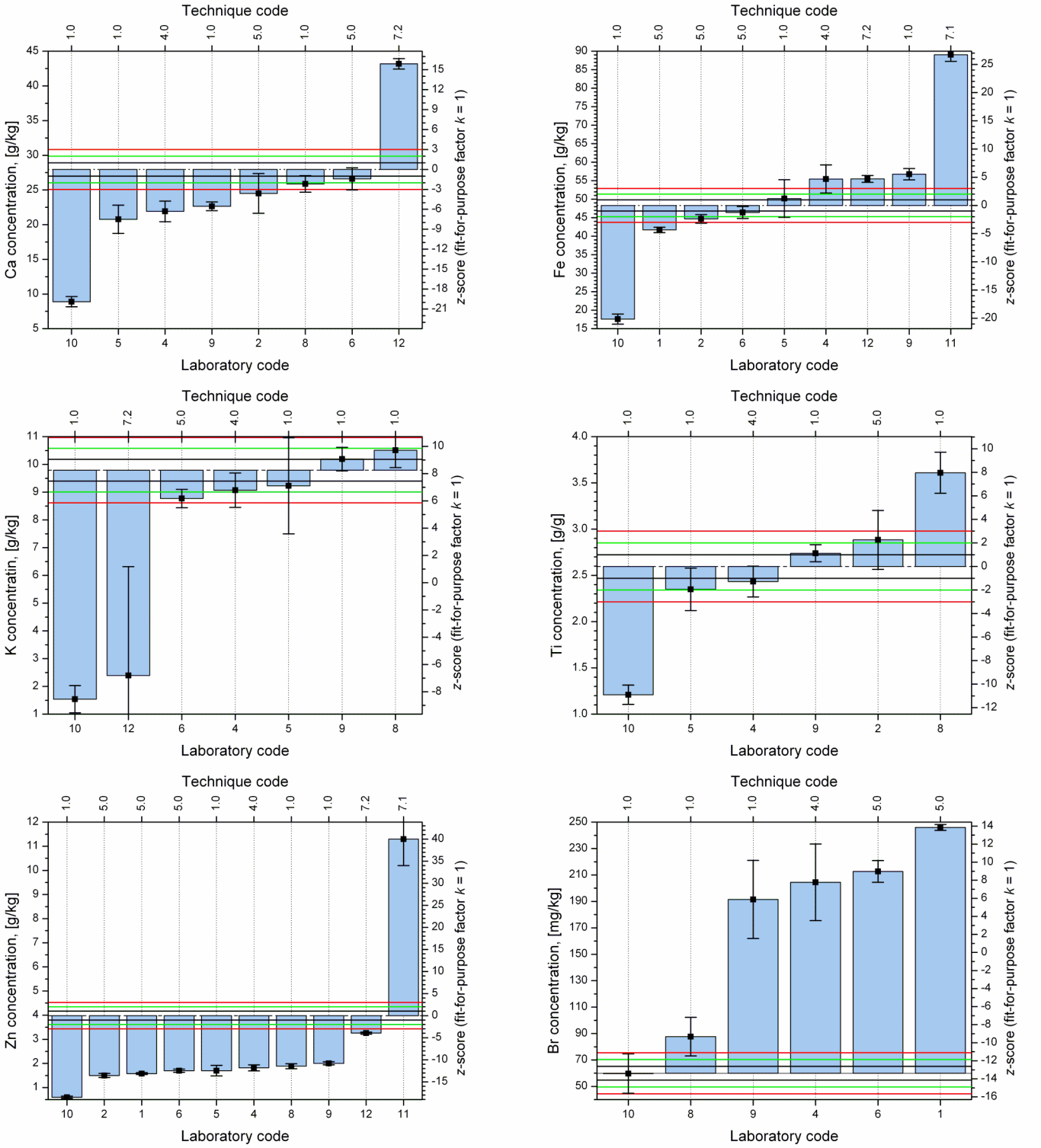
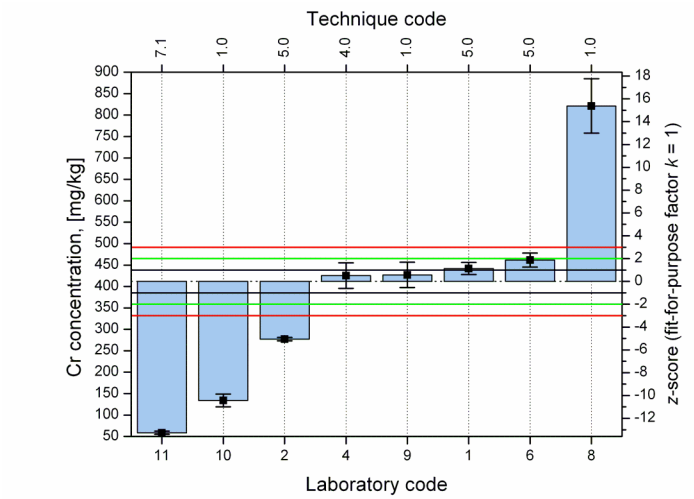
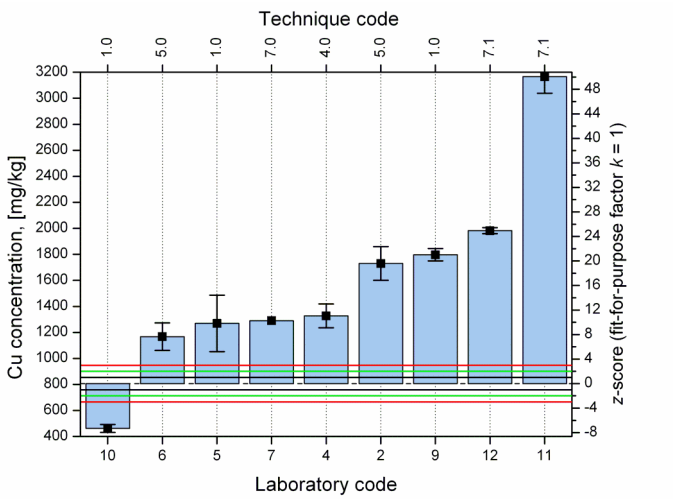
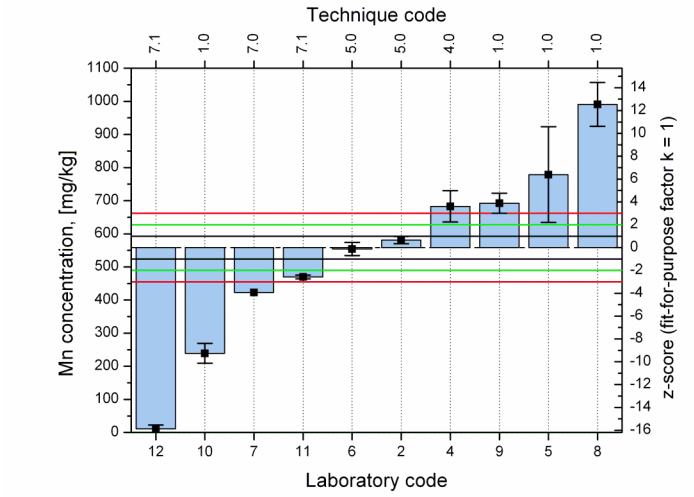


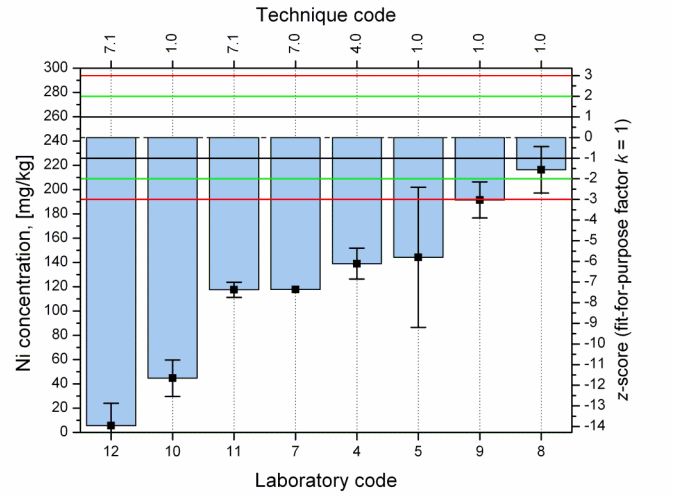
Fig. 4. Distributions of the *z*-scores for analytes reported by at least 6 laboratories. The bar charts show the distance between the reported and the assigned values of the analyte. The submitted results and their uncertainties, as provided by the analysts, are marked with filled squares accompanied by uncertainty bars. The horizontal lines show the admissible levels of *z*-score, $|z| < 2$, for three different fit-for-purpose ranges defined by factor *k* in Eqn. (2): ***k* = 0.5 - solid black lines**, ***k* = 1.0 - solid green lines**, and ***k* = 1.5 - solid red lines**.

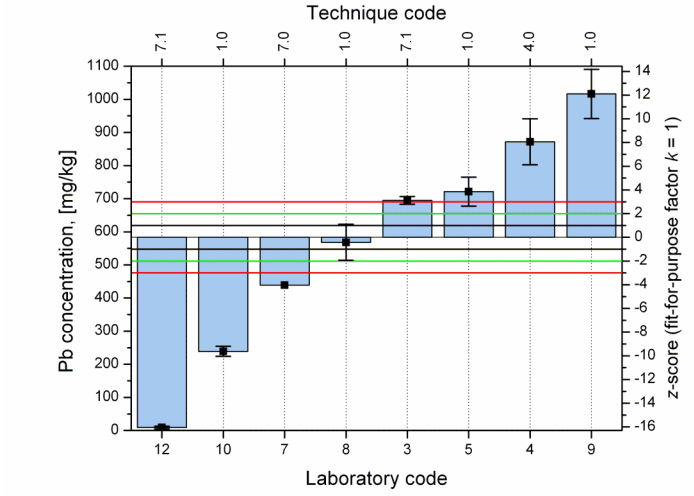
Fig. 4 continued…











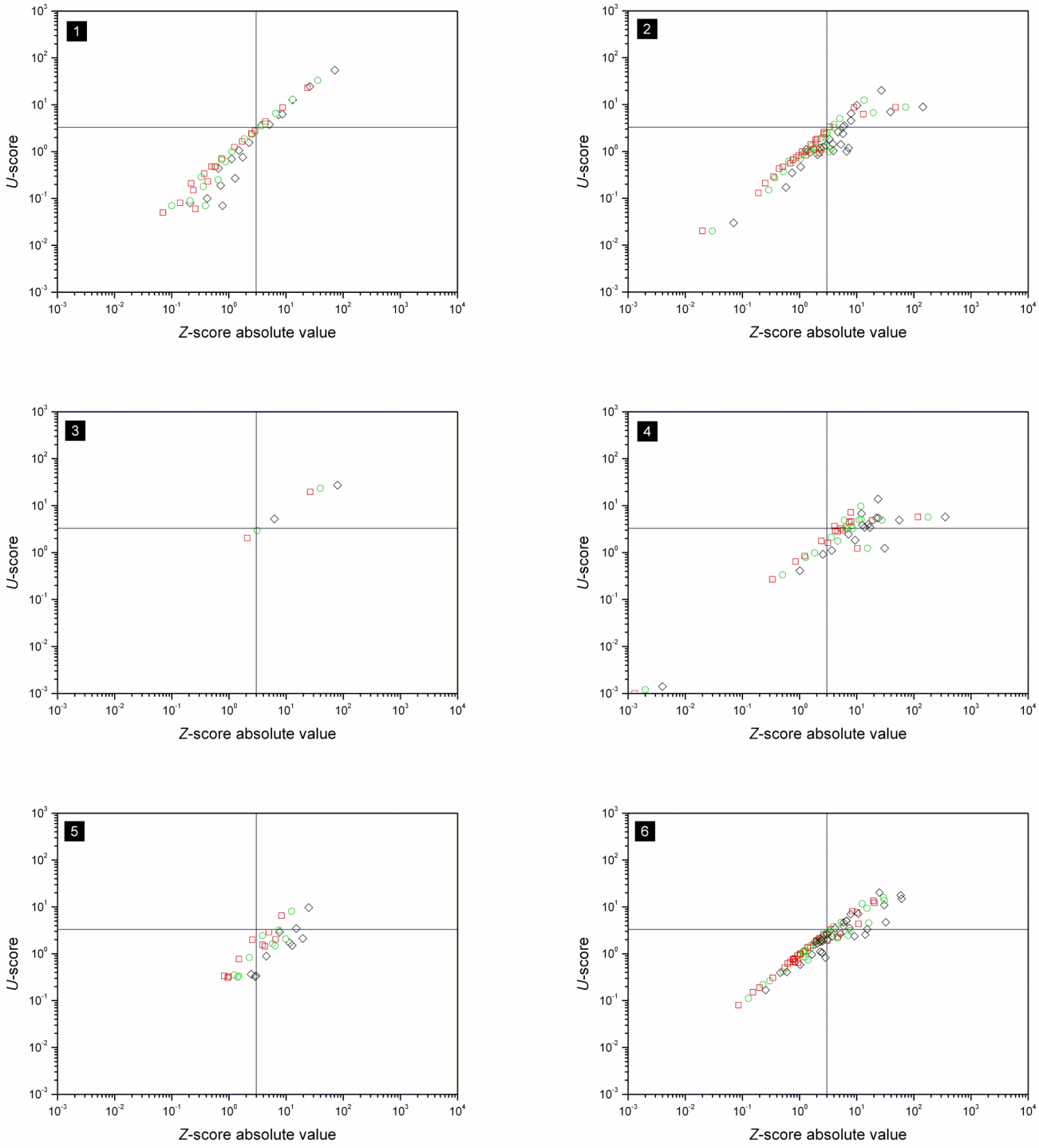
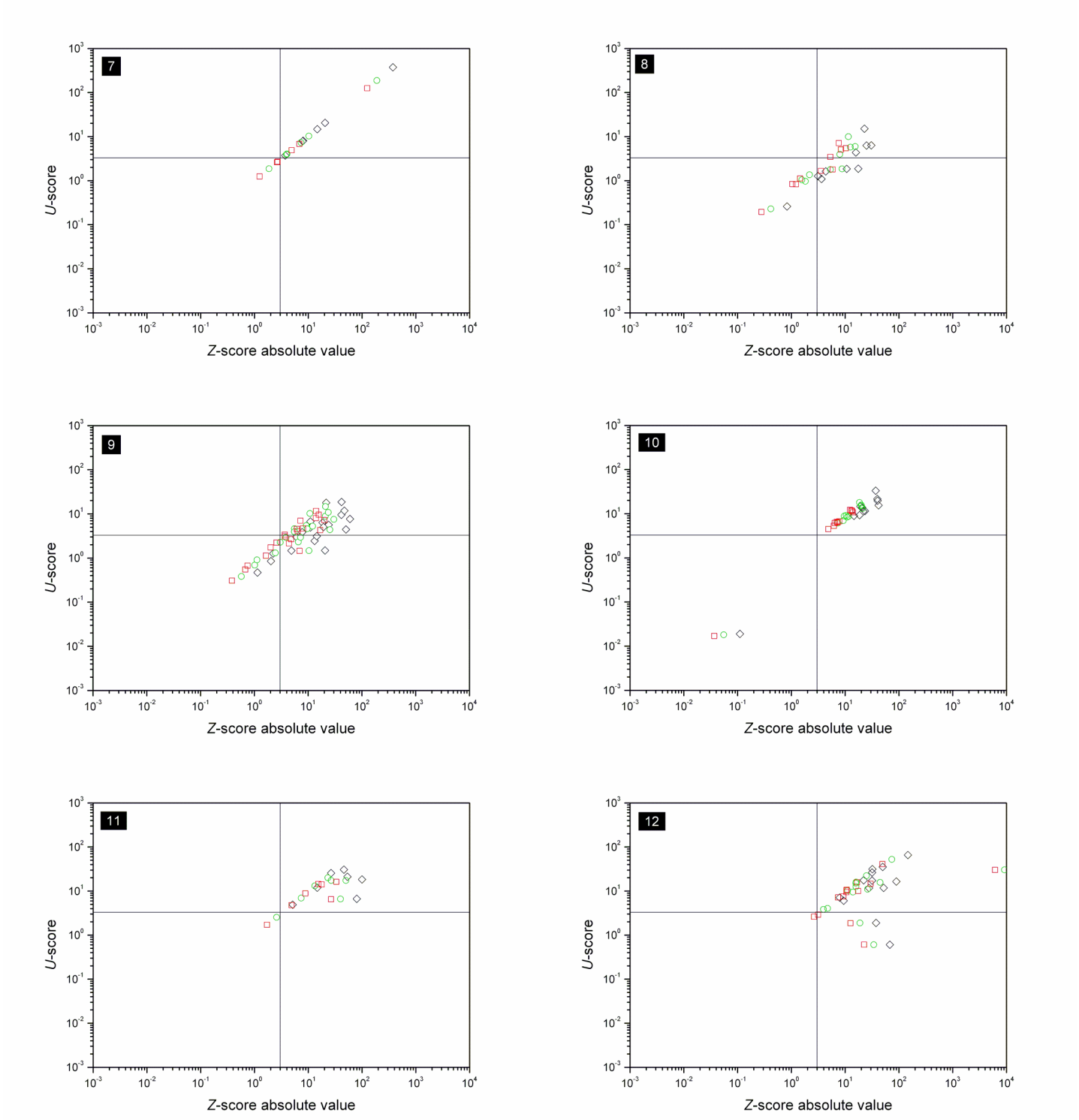


Fig. 5. Combined plots of *z*- and *u*-scores for participating laboratories. The laboratory code is shown in the left upper corner of each plot. The hollow symbols denote the values calculated for specific fit-for-purpose levels as defined in Eqn. (2) with factor *k*, namely: ***k* = 0.5 - black diamond symbols**, ***k* = 1.0 - green circle symbols**, and *k* = 1.5 - red square symbols. The solid lines mark the decision levels for *z*-score, $|z| = 3$, and *u*-score, *u* = 3.29.

Fig. 5 continued…



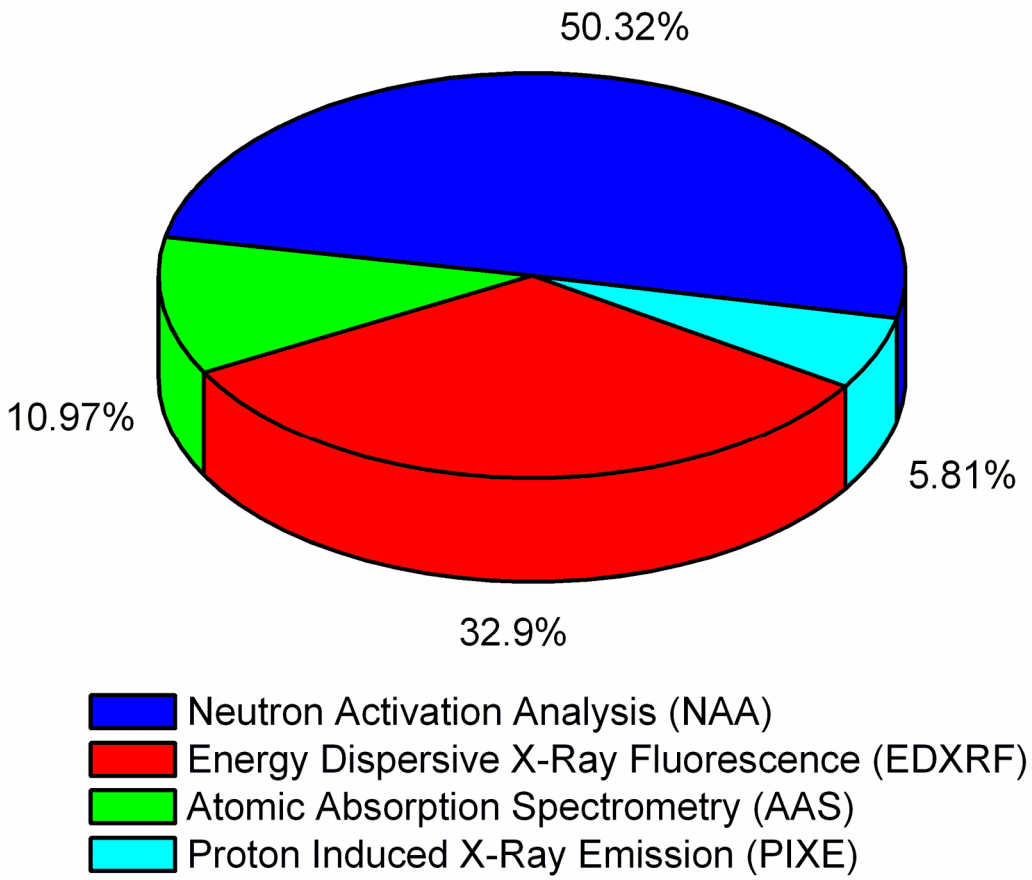


Fig. 6. Percentage utilization of the analytical techniques. The percent values refer to the total number of 175 submitted results.